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# Switchable Fermi surface sheets in greigite

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Greigite ( $\text{Fe}_3\text{S}_4$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) are isostructural and isoelectronic ferrimagnets with quite distinct properties. Electronic structure calculations reveal greigite is a normal metal in contrast to half-metallic magnetite. Greigite shows a complex Fermi surface with a unique influence of relativistic effects: The existence of sheets of the Fermi surface depends on the direction of the magnetization. This enables spinorbitronics, spintronics on the level of a single compound rather than a device. Due to its relativistic origin, spin contamination is irrelevant in spinorbitronics and the entire periodic table is available for optimizations.

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Magnetite has been known since ancient times. It occurs massively in nature and is the only known half-metallic magnet to do so. It orders ferrimagnetically with the moments of iron in the octahedral positions opposite to those in the tetrahedral positions. Below 120 K it transforms into an insulator.<sup>1</sup> The isostructural (spinel), isoelectronic mineral greigite ( $\text{Fe}_3\text{S}_4$ ) was discovered just half a century ago.<sup>2</sup> Parts of the deposits of greigite are biogenic, originating from magnetotactic or sulfur-reducing bacteria.<sup>3</sup> Greigite is metastable,<sup>4</sup> consequently its Curie temperature is not known from experiment. It can even be pyrophoric.<sup>5</sup> Because of its metastability it is difficult to obtain high quality samples and consequently not much is known about its physical properties. Recently the successful synthesis of greigite in the form of flowerlike microspheres was reported and proposed as a material for hydrogen-storage electrodes in nickel-metalhydride batteries.<sup>6</sup>

Here we report surprising results obtained in a larger, interdisciplinary study on the different role of magnetite and greigite in magnetoreception in biology. The calculated band structure of greigite shows an unusually high number of occurrences where majority-spin and minority-spin bands cross along high symmetry lines *very close* to the Fermi energy. Consequently, a large effect of the spin-orbit interaction is to be expected. This is remarkable. Usually the effect of spin-orbit coupling in solids is reduced by orbital quenching (chemical bonds eliminate orbital degeneracy), whereas in magnetic solids the absence of spin degeneracy reduces the spin-orbit interaction even further. Thus both chemical bonds and magnetism compete with the spin-orbit coupling and in all but heavy atoms the chemical bonding dominates. The band structure of greigite suggests that the situation is fundamentally different from ordinary solids and unusually large effects of spin-orbit interaction on the Fermi surface are to be expected. We emphasize that this is the result of the unique Fermi surface of greigite; the *strength* of the spin-orbit interaction is determined by the heaviest element (iron) and is consequently similar as in magnetite.

*Details of the calculations.* The calculations were carried out using the full-potential mixed linearized augmented plane wave (LAPW)/augmented plane wave + local orbitals (APW + lo) method<sup>7</sup> implemented in the WIEN2K code.<sup>8</sup> The exchange-correlation potential used the generalized gradient

approximation [Perdew-Burke-Ernzerhof (PBE)].<sup>9</sup> The experimental lattice parameters (9.88 Å for greigite and 9.394 Å for magnetite) were used. The positional parameter for the sulfur was determined as 0.2546, close to the experimental number (0.2505).<sup>10,11</sup> Convergence criteria were  $10^{-4}$  Ry ( $10^{-5}$  Ry in the relativistic case) for the energy and  $10^{-4}$   $e$  for the charge. An energy cutoff of  $R_{\text{mt}}K_{\text{max}}$  of 8 was used with a Brillouin-zone integration using 256  $k$  points in the irreducible part without spin-orbit interaction and equally dense meshes in the relativistic cases. Spin-orbit interaction was included in the calculations of the Fermi surfaces, using the second variational treatment.<sup>12</sup> The influence of spin-orbit interaction on the magnetic moments is negligible: a reduction of  $0.003\mu_B$  for the tetrahedral iron and  $0.006\mu_B$  for the octahedral site.

We compare the band structure of greigite with that of magnetite. Figures 1(a) and 1(b) show the band structure for the minority-spin direction for magnetite and greigite, respectively, in the vicinity of the Fermi level. For magnetite three bands intersect the Fermi energy. These bands are well separated from bands of iron  $d$  character at lower energy. The band structure of greigite appears more complex since the less electronegative sulfur  $p$  bands are positioned higher in energy compared with the oxygen bands in magnetite and form a rather covalent complex with the iron states. The dispersion of the three bands intersecting the Fermi energy and their overall bandwidths are quite similar, especially at the Brillouin-zone boundaries [the  $W$ ,  $K$  ( $U$ ), and  $L$  points as well as the lines connecting them]. The main difference is the presence of a band gap at the Fermi energy at the  $W$  and  $U$  points in case of greigite, where magnetite shows small band gaps around Fermi energy at  $K$  and  $U$  points in the Brillouin zone. The result is a different Fermi surface for the minority-spin channels of the two compounds. The situation for the majority-spin direction is fundamentally different: For magnetite a band gap exists at the Fermi energy [Fig. 1(c)], but in greigite [Fig. 1(d)] three energy bands intersect the Fermi energy. The dispersion of these bands is large compared with the minority-spin electrons: The majority spin shows a band structure of a good metal.

Experiments on greigite are rare and there is no indication for a Verwey-like transition in greigite. Our calculations show a strong similarity between the minority-spin electronic

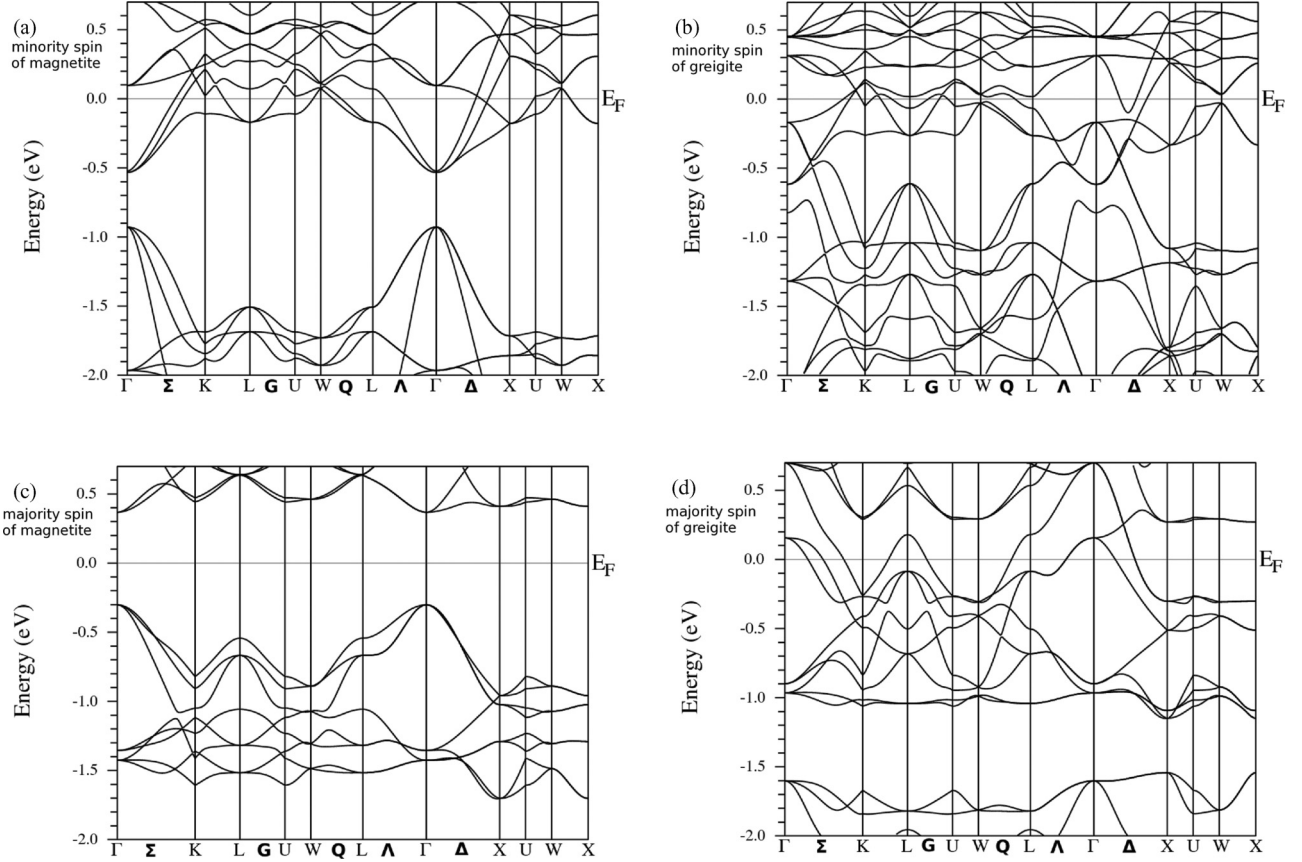


FIG. 1. Band structure for (a) the minority-spin direction of magnetite, (b) the minority-spin direction of greigite, (c) the majority-spin direction of magnetite, and (d) the majority-spin direction of greigite. The Fermi energy is at the zero of energy.

structure of magnetite and greigite, but for the majority spin the situation is strikingly different: semiconducting for magnetite and a good metal for greigite. Also, the reduced magnetic moments  $3.38\mu_B$  (in excellent agreement with the experimental value of  $3.35\mu_B$ ) with respect to  $4\mu_B$  in magnetite indicate a rather covalent situation in greigite. Consequently, no phenomena such as a Verwey transition or insulating behavior on a nanoscopic scale<sup>13,14</sup> are to be expected here. Our work is different from the recent calculation of Devey *et al.*,<sup>15</sup> where they obtain a half-metallic band structure with a magnetic moment of  $3.7\mu_B$  (with a Hubbard  $U$  of 1 eV), in conflict with the integer magnetic moment in any half metal.

We discuss the unique sensitivity of the Fermi surface of greigite for relativistic effects. In first order in  $(v/c)^2$ , three relativistic effects can be distinguished: the two scalar relativistic effects (mass velocity and Darwin terms) and the spin-orbit coupling. The last term is well known, but in condensed matter is seldom important (with exceptions, of course, for energetically small but qualitatively important effects such as the magneto-optical Kerr effect and magnetic anisotropy). This is because the orbital moment in condensed matter is in competition with the chemical bonding and the spin degeneracy is lifted in magnetic systems. Thus, in general, the effect of spin-orbit interaction in magnetic solids is greatly reduced as compared to isolated atoms. It is, however, still pronounced where bands of opposite spin cross (restoring spin degeneracy) and at high symmetry lines in the Brillouin

zone, where at least part of the symmetry of the isolated atom persists (orbital degeneracy). What makes the Fermi surface of greigite truly unique is the unusually high number of crossings of majority- and minority-spin bands along lines of high symmetry taking place at the Fermi energy. Indeed, five of these intersections are present: along the  $\Sigma$ ,  $\Delta$ ,  $Q$ , and  $G$  lines as well as along  $K$ - $L$  (equivalent to  $G$  in the second Brillouin zone), within millivolts of the Fermi energy. Consequently, one expects the Fermi surface to be sensitive for the effects of spin-orbit interaction in spite of the fact that greigite contains light elements only (relativistic effects scale with the fourth power of the nuclear charge). Figure 2 shows part of the three-dimensional (3D) Fermi surface [plotted by the visualization program XCRYSDEN 1.5.21 (Ref. 16)] for

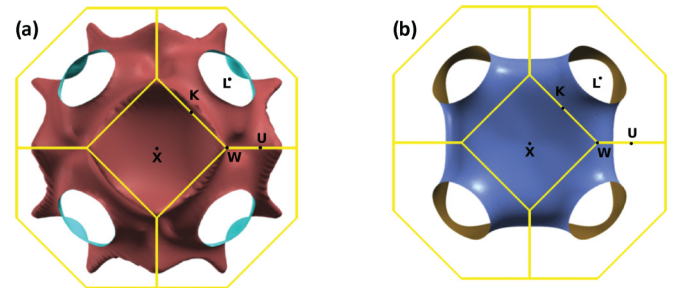


FIG. 2. (Color) Part of 3D Fermi surface of greigite. (a) The minority-spin direction; (b) the majority-spin direction.

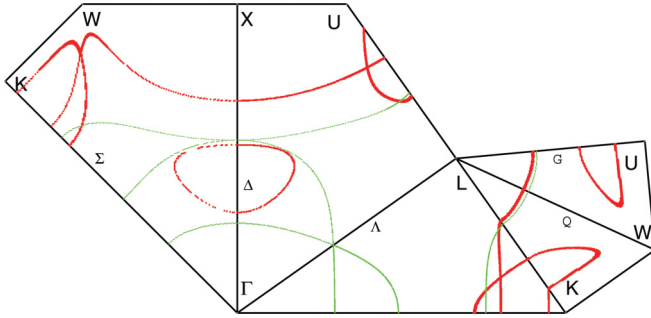


FIG. 3. (Color) Fermi surface of greigite without spin-orbit interaction. Majority spin: green and thin dots; minority spin: red and thick dots.

minority- and majority-spin directions for the nonrelativistic case. They both have necks, and the main difference is that the Fermi surface for the minority-spin direction is not nearly as smooth as the Fermi surface for the majority-spin direction, which confirms the band structure between minority- and majority-spin directions described above (for example, the large difference in dispersion along the  $L$ - $K$  line). Also, the neck along the  $\Gamma$ - $L$  line gives the answer to the appearance of two circular Fermi surface sheets in the  $LKWU$  planes in Fig. 3. In order to get detailed information, Fermi surfaces of greigite in some high symmetry planes of the first irreducible Brillouin zone are shown in Fig. 3 (for the nonrelativistic case), and Figs. 4 and 5 (both for the relativistic case). In Fig. 3, the Fermi surface for the majority-spin direction shows two  $\Gamma$ -centered sheets touching along the  $\Delta$  line with a third (open)  $\Gamma$ -centered sheet touching the second sheet along the  $\Delta$  line. The opposite spin direction has an isolated pocket along the  $\Delta$  line, an open  $\Gamma$ -centered sheet straddling a pocket along the  $G$  line, as well as an isolated pocket along the  $\Sigma$  line, open along the  $L$ - $K$  line.

The Fermi surface for the relativistic case depends on the spin-quantization axis. The Fermi surface with the spin-quantization axis along the  $[100]$  direction (the easy axis of greigite<sup>17</sup>) is shown in Fig. 4. The smallest  $\Gamma$ -centered sheet is unaffected, but the second majority-spin sheet and the minority isolated pocket along the  $\Delta$  line have collapsed into a single sheet. Sheets closer to the zone boundaries are broken up into individual pieces: a curved disklike shaped surface along the  $\Delta$  line, a small saucer around  $\Sigma$  as well as a bigger one extending into the second zone, another one along the  $G$  line, and finally a similar object in the  $\Gamma$ - $K$ - $L$  plane, not connected to a high symmetry line. The spin-orbit

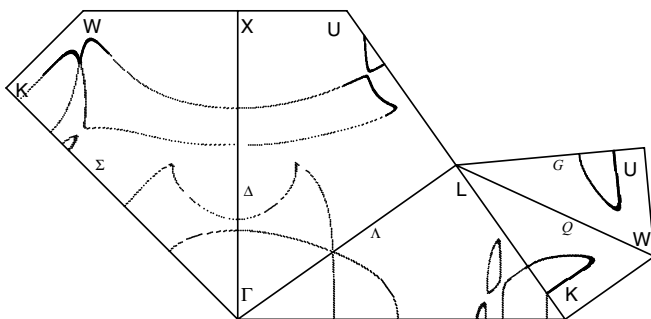


FIG. 4. Fermi surface of greigite with spin-orbit interaction and magnetization//[100].

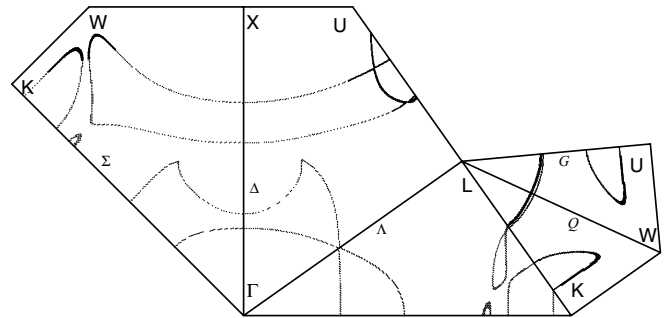


FIG. 5. Fermi surface of greigite with spin-orbit interaction and magnetization//[111], noticing that these two circular Fermi surface sheets are quite near in the  $LKWU$  plane.

interaction has eliminated *three Fermi surface sheets*: One mentioned already along  $\Delta$  and two intersections along  $Q$  have disappeared, eliminating the two  $L$ -centered circular sheets (which are clearly shown in Fig. 2). The Fermi surface for the spin quantization along the  $[001]$  direction is very similar: The only qualitative difference is a minisheet just touching  $1/3$  along  $Q$ . The Fermi surface with the  $[111]$  direction as the quantization axis is shown in Fig. 5. Compared to the Fermi surface (with magnetization along the  $[100]$  direction), in the  $\Gamma XUL$  plane, especially around the  $L$ - $U$  line, a large difference occurs. More importantly, in the  $LKWU$  plane, the two circular sheets *reappear* in this direction of the magnetization. To the best of our knowledge this is the first example of a material where complete sheets of the Fermi surface can be switched on and off by just changing the direction of the magnetization.

Recently, much interest is seen in the field of spintronics. Here the electronic conduction of a device consisting of two electrodes of a material with distinct transport properties for the two spin directions (ideally a half metal) depends sensitively on the orientation of the magnetization of the electrodes with respect to each other.<sup>18</sup> The phenomenon reported here could lead to similar behavior by switching the properties in a *single* material. Giant magnetoresistance (GMR) depends on the difference in spin direction of two geometrically different layers. Spin-orbit interaction mixes states with different spin directions and hence is detrimental. Consequently GMR is limited to materials with relatively low nuclear charge. Also, spin degeneracies and orbital degeneracies in the vicinity of the Fermi energy are detrimental. Spin purity is of no concern in spinorbitronics, however, since it is based on *one* homogeneous layer; consequently the complete periodic table is available for optimizations (chemical stability, Curie or Néel temperature, strength of spin-orbit interaction, etc.). This is an important point: In greigite the size of the spin-orbit interaction limits the range of operating temperature to 200 K. It is difficult to synthesize a high quality single crystal of metastable greigite. Future developments in spinorbitronics require the synthesis of a high quality single crystal of greigite, and other materials with similar properties.

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